Modification of the Supercritical Temperature-dependent Attractive Parameter of a Simplified Perturbed Hard Sphere Equation of State

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A quartic perturbed hard-sphere equation of state (QPHS EOS) employing a simplified hard-sphere repulsive term proposed by Scott has been developed. Following the approach introduced by Wilson and popularized by Soave, the temperature dependence of the parameter *a(T)* has been fitted to enable the equation to reproduce vapor pressures accurately.

The possible improvement is to have separate functions of *a(T)* for the subcritical and the supercritical temperatures. An exponential form will ensure that the supercritical *a(T)* would vanish as temperature approaches infinity. The experimental data of Shirota and Srago suggests that the slope of the vapor pressure curve at the critical point is the same as that of the curve formed by the loci of the $c_p(T)$ maxima. By equating the first and the second derivatives of *a(T)* with respect to temperature, the supercritical function retains one of the three constants obtained from the vapor pressure fit.

In this study, an exponential form is regressed to 56 c_p maxima data points of selected pure fluids compiled by Kim, consisting of c_p^M (heat capacity values) and T_r^M (reduced temperatures) of the c_p maxima data). To test the effectiveness of this approach, the constants obtained from the pure fluids regression were used to calculate heat capacity of n-pentane-acetone and methanol-acetone binary mixtures at supercritical temperatures. This approach was found to improve prediction of location of pure-fluids c_p maxima but not its magnitude. Although an entirely new type of EOS is needed to reduce the deviations in c_p^M, it is found that the deviations in T_r^M can be reduced by using an additional parameter in the expression for supercritical *a(T)*. The total absolute deviations in T_r^M calculated using the QPHS EOS is about one-half of those of Peng-Robinson EOS. The proposed modification can be translated into improvement in heat capacity calculations only if the crossover problem (incorporating both classical and non-classical behavior of fluids in the critical region into a single EOS) is solved.